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# Coupled spin-charge dynamics in $\text{NaV}_2\text{O}_5$ and its effect on the optical absorption

M. V. Mostovoy, D. I. Khomskii, and J. Knoester

*Theoretical Physics Institute and Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

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We argue that in the quarter filled ladder compound  $\text{NaV}_2\text{O}_5$  the quasi-one-dimensional spin system is strongly coupled to an antiferroelectric mode with a broad band. This mode is the single-electron excitation on a rung of the two-leg ladder, which can hop from rung to rung due to the Coulomb interactions between electrons. We show that the coupling of the antiferroelectric mode to spins gives rise to the infrared absorption continuum, observed in  $\text{NaV}_2\text{O}_5$ .

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## I. INTRODUCTION

Sodium vanadate ( $\text{NaV}_2\text{O}_5$ ), first studied in the 1970s,<sup>1</sup> has become an object of intensive experimental and theoretical investigations after the discovery of the phase transition at  $T_c = 34$  K.<sup>2</sup> Several physical concepts, such as bipolarons,<sup>3</sup> spin-Peierls transition,<sup>2,4</sup> and charge ordering,<sup>5-8</sup> have been proposed to explain the properties of this material. Yet, despite all the efforts, the real structure of sodium vanadate and especially the nature of the low-energy excitations in it are still poorly understood.

In  $\alpha'$ - $\text{NaV}_2\text{O}_5$  the vanadium ions form two-leg ladders organized in layers (see Fig. 1). Until recently it was assumed that the vanadium ladders with one electron per rung are equivalent to spin- $\frac{1}{2}$  chains, so that sodium vanadate is a quasi-one-dimensional spin system. Indeed, this material is a good insulator and its magnetic susceptibility has temperature behavior similar to that of the Heisenberg spin- $\frac{1}{2}$  chain with the exchange constant  $J \sim 560$  K.<sup>9</sup> At  $T_c = 34$  K sodium vanadate undergoes a phase transition into a state with a spin gap. Below  $T_c$  the lattice period along the ladders ( $b$  direction) and perpendicular to ladders within the layers ( $a$  direction) doubles, while the period in the direction perpendicular to the layers ( $c$  direction) increases by a factor of 4.<sup>4</sup> The transition was initially interpreted as a spin-Peierls transition, driven by the instability of spin- $\frac{1}{2}$  chains against the formation of local dimers.

However, the strong suppression of  $T_c$  by magnetic field, characteristic for spin-Peierls systems, was not found in sodium vanadate.<sup>10,11</sup> Furthermore, the entropy released at the transition in  $\text{NaV}_2\text{O}_5$  is considerably higher than the expected release of the spin entropy.<sup>9-11</sup> These results indicate that the energy gain due to the spin-gap opening is not the main reason for the phase transition in this material and that other degrees of freedom are involved.

This conclusion is consistent with recent x-ray<sup>12-14</sup> and NMR (Ref. 5) measurements, which show that above  $T_c$  all vanadium ions are equivalent ( $\text{V}^{4.5+}$ ), whereas below  $T_c$ , a charge disproportionation occurs. There is, however, still a controversy about the number of distinct V sites and their arrangement in the low-temperature phase.<sup>5,15-17</sup>

It was suggested that the driving force of the phase transition is the charge ordering of electrons in the quarter filled vanadium ladders and that the spin gap opens due to alternation of the spin-exchange constants, resulting from the

charge ordering.<sup>6,8</sup> Since sodium vanadate is an insulator both above and below  $T_c$ , the charge ordering is actually an (anti)ferroelectric transition. The electric dipoles that become ordered at this transition are located on the rungs of the vanadium two-leg ladders, predominantly occupied by one electron.<sup>8</sup> The available experimental data, e.g., the anomalous x-ray scattering<sup>18</sup> and the studies of the anomaly in the dielectric susceptibility close to  $T_c$ ,<sup>19-21</sup> indicate that in the ordered phase the directions of the dipoles alternate along the ladders, corresponding to a zigzag ordering of electron charges. In Ref. 8 we showed that the antiferroelectric ordering of dipoles in the system of vanadium ladders opens a spin gap.

In sodium vanadate the amplitude of the electron hopping along the rungs of the vanadium ladders, which plays the role of the tunneling amplitude between two states of the electric dipole, is of the same order as the Coulomb interaction between electrons on neighboring rungs that is responsible for the charge ordering. Thus the quantum nature of the dynamics of the electric dipoles in sodium vanadate cannot be ignored. This dynamics gives rise to a branch of excita-

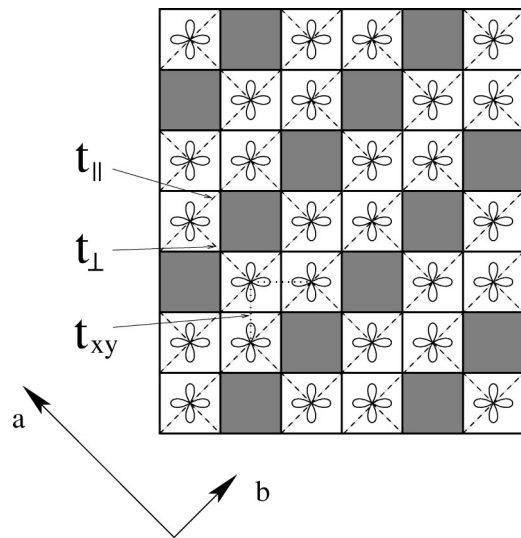


FIG. 1. The crystal structure of the V-O plane in  $\text{NaV}_2\text{O}_5$ : oxygens are located at the corners of the plaquettes, while V ions are located at their centers; the shaded plaquettes are vacant. Also shown are the vanadium ladders (dashed lines) and the relevant  $d_{xy}$  orbitals of the V ions.

tions that correspond to dipole flips propagating from one unit cell to another. The ordering of dipoles is accompanied by the softening of these excitations.<sup>22</sup> The softening occurs at the wave vector of the superlattice structure appearing in the ordered phase. For the antiferroelectric ordering (see Sec. III) the soft mode has a nonzero wave vector and therefore cannot be directly excited in optical absorption and Raman scattering above the transition temperature. Nevertheless, we show in this paper that the optical data do provide evidence for the presence of low-energy charge excitations in sodium vanadate.

The optical spectrum of sodium vanadate contains a broad absorption band covering almost the entire midinfrared region of frequencies.<sup>23–25</sup> A broad peak was observed also in Raman experiments.<sup>25–27</sup> In this paper we explain the low-frequency optical absorption in sodium vanadate by the photoexcitation of a three-particle continuum: two spinons plus a low-energy charge excitation. Our mechanism crucially depends on both the presence of the soft antiferroelectric mode, associated with the charge ordering, and on the coupling of this mode to the spin excitations.

This coupling naturally arises in the spin-isospin model of sodium vanadate discussed in Sec. II. The low-energy charge excitations and their softening at the transition temperature are considered in Sec. III. In Sec. IV we consider the absorption in the pure isospin model, describing only the charge excitations. We show that a low-frequency photon cannot excite three charge excitations. The low-energy absorption spectrum due to the photoexcitation of one charge excitation and two spinons is calculated and compared to experiment in Sec. V. Finally, we discuss our results in the concluding Sec. VI.

## II. SPIN-ISOSPIN MODEL

The experimental observations mentioned in Sec. I indicate that the low-temperature properties of sodium vanadate cannot be described by only considering the spin and lattice dynamics, but that it is necessary to include also the charge degrees of freedom. On the other hand, sodium vanadate is known to be a good insulator, both above and below  $T_c$ . We therefore argued in Ref. 8 that the relevant electronic excitations in this material are excitons. In this section we briefly discuss the “spin-isospin” model, introduced in Ref. 8 which describes the low-energy excitations in sodium vanadate.

In that model we restrict ourselves to the states with only one electron per rung of the vanadium ladder. This was suggested by Smolinski *et al.* on the basis of LDA calculations,<sup>13</sup> which show that the electron hopping amplitude along rungs  $t_\perp$  is significantly higher than the amplitudes of hopping between the sites of different rungs (of which the largest is the hopping amplitude along ladders  $t_\parallel$ ). If one first neglects the interrung hopping and the interrung electron-electron interactions, then on each rung of the quarter filled vanadium ladder there is one electron occupying the symmetric bonding state with energy  $-t_\perp$ . Due to the large value of the on-site Coulomb repulsion (which we assume to be infinite), an electron can hop only to an empty site of a neighboring rung. Then the hopping to a neighboring rung

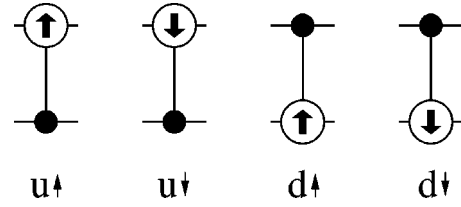


FIG. 2. The four different states of a single electron on a rung represented as the eigenstates of the spin  $S=\frac{1}{2}$  and the isospin  $T=\frac{1}{2}$  operators. The open circle denotes the position of the electron, the arrow its spin projection.

results in an energy increase  $2t_\perp$ . Thus the quarter filled two-leg ladder becomes equivalent to the half filled Hubbard chain with an effective “on-rung” repulsion  $U_r=2t_\perp$ .

This explains, in principle, why vanadium ladders are insulating. However, for the values of the hopping amplitudes, obtained in Ref. 13,  $t_\perp=0.38$  eV and  $t_\parallel=0.17$  eV, the width of the one-dimensional band  $4t_\parallel$  is comparable with  $U_r$ . Thus the charge fluctuations on the ladder rungs are not small and treating the vanadium ladder as a spin chain, as it was done in Ref. 13, is not well justified.

The situation improves if we take into account the Coulomb interactions between electrons on different rungs. The latter lead to an increase of the value of the “on-rung” repulsion. For instance, if we include the repulsion between the nearest-neighbor sites in ladders,  $V$ , then  $U_r \approx 2t_\perp + V/2$ , for small  $V$ . In general, the interrung Coulomb interactions make  $U_r$  not a well-defined quantity, as it becomes dependent on the positions of many electrons.

Thus, on the one hand, the interrung Coulomb interactions help to justify the assumption of one electron per rung. On the other hand, they strongly mix the symmetric and anti-symmetric states on each rung, as the typical value of such interactions is of the same order as the energy separation between these two states,  $2t_\perp \approx 0.75$  eV. Thus the electron position on a rung becomes an important additional degree of freedom, which makes the vanadium ladder different from a spin chain.

The two states,  $u_n$  and  $d_n$ , corresponding to the two possible positions of a single electron on the rung  $n$ , can be described as the up and down eigenstates of an isospin- $\frac{1}{2}$  operator  $T_n^z$ . With two spin projections there are in total four different states of an electron on a rung (see Fig. 2). The spin  $S_n$  and the isospin  $T_n$  are defined on a lattice, the sites of which correspond to the rungs of vanadium ladders (see Fig. 3). In this paper we ignore the three-dimensional structure of sodium vanadate and only consider one oxygen-vanadium layer. Then the lattice of our model is triangular. Furthermore, for our considerations it will not be important that in each layer the orientations of the oxygen pyramids, surrounding V ions, in the nearest-neighbor ladders are opposite to each other (which is why the unit cell above  $T_c$  contains two ladders). Therefore we choose  $\mathbf{f}_1=\mathbf{b}$  and  $\mathbf{f}_2=\frac{1}{2}(\mathbf{a}+\mathbf{b})$  as the basis of the unit cell in the high-temperature phase.

The charge part of the Hamiltonian of the model, which only includes the isospin operators, has the form

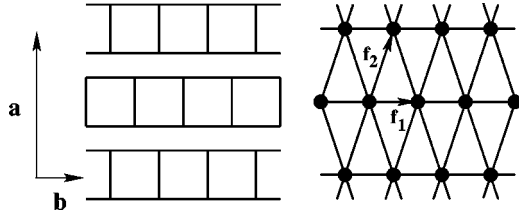


FIG. 3. From vanadium ladders (left-hand side of the picture) to the effective lattice (right-hand side of the picture). The sites of the latter should be identified with the centers of the rungs of the V ladders.

$$H_T = -2t_{\perp} \sum_{\mathbf{n}} T_{\mathbf{n}}^x + \frac{1}{2} \sum_{\mathbf{nm}} V_{\mathbf{nm}} T_{\mathbf{n}}^z T_{\mathbf{m}}^z, \quad (1)$$

where  $t_{\perp}$  is the amplitude of electron hopping along the ladder rungs and the second term describes the Coulomb interaction between electrons on different rungs. The amplitudes  $V_{\mathbf{nm}}$  are defined by

$$V_{\mathbf{nm}} = V(u_{\mathbf{n}}, u_{\mathbf{m}}) + V(d_{\mathbf{n}}, d_{\mathbf{m}}) - V(u_{\mathbf{n}}, d_{\mathbf{m}}) - V(d_{\mathbf{n}}, u_{\mathbf{m}}), \quad (2)$$

where, e.g.,  $V(u_{\mathbf{n}}, d_{\mathbf{m}})$  is the energy of the Coulomb interaction between an electron on rung  $\mathbf{n}$  in the up state and an electron on rung  $\mathbf{m}$  in the down state. For large distances between rungs,  $V_{\mathbf{nm}}$  has the form of the dipole-dipole interaction. These interactions favor a certain charge ordering, which in our model corresponds to an ordering of the  $z$  projections of the isospins, while the electron hopping counteracts the ordering. Since the hopping term does not commute with the Coulomb term, the isospins are quantum (rather than classical) degrees of freedom, like the orbital degrees of freedom in Mott insulators with orbital degeneracy.<sup>28</sup>

We now turn to the spin contributions to the Hamiltonian. The spin exchange results from virtual hopping of electrons between neighboring rungs, and the exchange interaction is the strongest in the ladder direction. For the half filled Hubbard chain the exchange interactions between spins on two neighboring sites has the form  $(2t^2/U)S_{12}$ , where  $S_{12} = 2(\mathbf{S}_1 \cdot \mathbf{S}_2) + \frac{1}{2}$  is the operator that exchanges  $\mathbf{S}_1$  with  $\mathbf{S}_2$ . In the two-leg ladder it is possible to have in the intermediate state a doubly occupied rung without doubly occupied sites. Thus even for infinite  $U$  the exchange coupling is nonzero and  $U$  has to be replaced by the “on-rung” repulsion  $U_r$ . In the infinite  $U$  case the exchange of spins necessarily involves the exchange of the  $z$  projections of the isospins on two neighboring rungs ( $u_1 d_2 \leftrightarrow d_1 u_2$ ), so the spin-exchange interaction has the form:  $(2t^2/U_r)S_{12}(T_1^+ T_2^- + T_1^- T_2^+)$ . Thus instead of a pure spin-exchange Hamiltonian we obtain a spin-isospin interaction:

$$H_{ST}^{(1)} = A \sum_{\mathbf{n}} (\mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}+\mathbf{f}_1}) (T_{\mathbf{n}}^x T_{\mathbf{n}+\mathbf{f}_1}^x + T_{\mathbf{n}}^y T_{\mathbf{n}+\mathbf{f}_1}^y). \quad (3)$$

Here the rungs  $\mathbf{n}$  and  $\mathbf{n}+\mathbf{f}_1$  are two nearest-neighbor rungs of the ladder (see Fig. 3) and the interaction amplitude  $A = 8t_{\perp}^2/U_r$ ,  $U_r$  being the effective “on-rung” Coulomb repulsion discussed above.

We note that Eq. (3) gives only an approximate description of the spin-isospin interaction in sodium vanadate, because in the presence of interrung Coulomb interactions, both initial and intermediate states in the spin-exchange process are complicated many-electron states, so that the increase of the energy in the virtual state cannot be described by a single constant  $U_r$ . However, Eq. (3) contains many basic ingredients, necessary for a qualitative description of the properties of sodium vanadate. In particular, treating the spin-isospin interaction in the mean-field approximation we obtain the effective spin-exchange coupling constant,

$$J = A \langle T_{\mathbf{n}}^x T_{\mathbf{n}+\mathbf{f}_1}^x + T_{\mathbf{n}}^y T_{\mathbf{n}+\mathbf{f}_1}^y \rangle, \quad (4)$$

where the brackets denote the thermal and quantum average of the isospin operators. The exchange coupling is therefore temperature dependent, which may account for the deviation of the magnetic susceptibility of sodium vanadate from the Bonner-Fisher curve.<sup>11,29</sup> Using the Hamiltonian Eq. (1), one can show that, above  $T_c$ , the exchange coupling increases as the temperature decreases, which is in agreement with the conclusion of Ref. 29, where such an increase was introduced phenomenologically in order to reconcile the magnetic susceptibility data for  $\text{NaV}_2\text{O}_5$  with the temperature dependence of the magnetic susceptibility of the Heisenberg spin- $\frac{1}{2}$  chain.

However, there is one very important effect of the electronic charge distribution on the spin exchange that is not described by Eq. (3). Namely, the Hamiltonian Eq. (3) does not explain the spin-gap opening due to the zigzag charge ordering. In order to find the term in the spin-isospin interaction responsible for the spin gap opening, we note that the exchange between spins on rungs  $\mathbf{n}$  and  $\mathbf{n}+\mathbf{f}_1$  depends on the position of electrons in the nearest rungs of the two neighboring ladders,  $\mathbf{n}+\mathbf{f}_2$  and  $\mathbf{n}+\mathbf{f}_1-\mathbf{f}_2$  (see Fig. 3). Roughly speaking, electrons affect the hopping amplitudes between the rungs of nearest-neighbor ladders, which in turn, affect the spin exchange. The corresponding Hamiltonian describing such an influence has the form

$$H_{ST}^{(2)} = B \sum_{\mathbf{n}} (T_{\mathbf{n}+\mathbf{f}_2}^z - T_{\mathbf{n}+\mathbf{f}_1-\mathbf{f}_2}^z) (\mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}+\mathbf{f}_1}). \quad (5)$$

As was argued in Ref. 8, this interaction is responsible for the opening of the spin gap in the charge ordered phase. Indeed, for the zigzag structure with a doubling of the period in the  $a$  and  $b$  directions [see Fig. 5(a) below], the exchange alternates along ladders, which opens a spin gap.

To end this section, we note that the virtual hopping of electrons on neighboring rungs, apart from affecting the spin exchange, also results in corrections to the pure isospin Hamiltonian Eq. (1), which we neglect here, as they are relatively small. Furthermore, for large, but finite on-site Hubbard  $U$ , one obtains also the spin-isospin interaction term of the form

$$H_{ST}^{(3)} = A' \sum_{\mathbf{n}} (\mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}+\mathbf{f}_1}) T_{\mathbf{n}}^z T_{\mathbf{n}+\mathbf{f}_1}^z, \quad (6)$$

where  $A' \propto t_{\perp}^2/U$ .



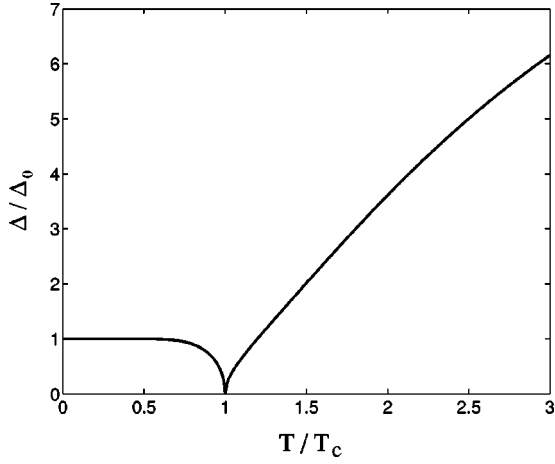


FIG. 4. Temperature dependence of the isospin gap  $\Delta$ . The value of  $|V(\mathbf{Q})|$ , used for this calculation, is close to its quantum critical value  $2t_\perp$ , so that the isospin gap  $\Delta \ll 2t_\perp$ .

### III. ISOSPIN EXCITATIONS

In this section we discuss the charge (isospin) excitations for the pure isospin Hamiltonian (1). These excitations may be viewed as Frenkel excitons. Indeed, the rotation over  $\pi/2$  around the  $y$  axis in the isospin space:  $T^x \rightarrow T'^z$  and  $T^z \rightarrow -T'^x$ , transforms Eq. (1) into the familiar Frenkel exciton Hamiltonian,

$$H_T = -2t_\perp \sum_{\mathbf{n}} T'^z_{\mathbf{n}} + \frac{1}{2} \sum_{\mathbf{nm}} V_{\mathbf{nm}} T'^x_{\mathbf{n}} T'^x_{\mathbf{m}}. \quad (7)$$

In the rotated basis, the isospin flip:  $|\uparrow\rangle \rightarrow |\downarrow\rangle$  corresponds to the electronic excitation of a single rung from the symmetric state with energy  $-t_\perp$  to the antisymmetric state with energy  $+t_\perp$ . The second term in Eq. (7), describing the Coulomb interactions between electrons, gives rise to the hopping of the excitation from the rung  $\mathbf{n}$  to the rung  $\mathbf{m}$  with the hopping amplitude  $V_{\mathbf{nm}}$ .

The dispersion of these excitations can be found by considering the retarded Green function

$$\langle\langle T^z | T^z \rangle\rangle_{\omega, \mathbf{q}} = -i \int_0^\infty dt e^{i(\omega + i\delta)t} \sum_{\mathbf{n}} e^{-i\mathbf{q} \cdot \mathbf{x}_n} \langle [T^z(t), T^z(0)] \rangle \quad (8)$$

(here we use the original basis in the isospace). This Green function is calculated in the random phase approximation (RPA) in Appendix A. In the disordered phase it is given by

$$\langle\langle T^z | T^z \rangle\rangle_{\omega, \mathbf{q}} = \frac{2t_\perp M^x}{(\omega^2 - E_q^2 + i\delta \text{sgn} \omega)}, \quad (9)$$

where  $M^x = \langle T^x \rangle$  and  $E_q$  is the energy of the isospin excitation with wave vector  $\mathbf{q}$  (at which the RPA Green function has a pole):

$$E_q = \sqrt{2t_\perp [2t_\perp + M^x V(\mathbf{q})]}. \quad (10)$$

Here  $V(\mathbf{q})$  is the Fourier transform of the interaction  $V_{\mathbf{nm}}$ , defined by Eqs. (1) and (2).

The wave vector  $\mathbf{q} = \mathbf{Q}$ , at which the bottom of the exciton band is reached, determines the type of the isospin ordering below the critical temperature  $T = T_c$ . The ordered state of the isospin system is characterized by a nonzero value of  $M^z = \langle T^z_{\mathbf{n}} \rangle$ . The ordering of isospins in the  $z$  direction corresponds to the modulation of the electronic density on the rungs of the vanadium ladders. The wave vector of the modulation equals  $\mathbf{Q}$

$$\langle T^z_{\mathbf{n}} \rangle = e^{i\mathbf{Q} \cdot \mathbf{x}_n} M^z. \quad (11)$$

The temperature dependence of  $M^x$  and  $M^z$  can be found from the mean-field equations

$$\begin{cases} M^z [2t_\perp + M^x V(\mathbf{Q})] = 0, \\ \sqrt{(M^x)^2 + (M^z)^2} = \frac{1}{2} \tanh \frac{\sqrt{(2t_\perp)^2 + [V(\mathbf{Q})M^z]^2}}{2T}. \end{cases} \quad (12)$$

Then the equation for the critical temperature, below which  $M^z$  (the amplitude of the charge modulation with the wave vector  $\mathbf{Q}$ ) becomes nonzero, is

$$2t_\perp + M^x(T_c) V(\mathbf{Q}) = 0, \quad (13)$$

where  $M^x(T_c) = \frac{1}{2} \tanh(t_\perp/T_c)$ . From Eqs. (10) and (13) we find that at the critical temperature the exciton gap  $\Delta = E_{\mathbf{Q}}$  becomes zero.

Since the appearance of a finite value of  $\langle T^z_{\mathbf{n}} \rangle \neq 0$  below  $T_c$  corresponds to a nonzero dipole moment on the rung  $\mathbf{n}$ , the ordering of isospins is an (anti)ferroelectric transition. The softening of the mode, describing the collective charge fluctuations, at the critical temperature is a well-known property of displacive (anti)ferroelectric transitions.

Below  $T_c$  the energy of the isospin excitation is given by (see Appendix A)

$$E_q = \sqrt{2t_\perp [2t_\perp + M^x V(\mathbf{q})] + |V(\mathbf{Q}) M^z|^2}. \quad (14)$$

Using Eq. (12) we obtain

$$\Delta = |V(\mathbf{Q}) M^z|.$$

Thus the isospin gap reappears in the ordered state. The typical temperature dependence of the isospin gap is shown in Fig. 4.

Clearly if  $V_{\mathbf{nm}}$  is known, the charge ordering vector  $\mathbf{Q}$  can be in principle be found. However, simple estimates show that different ordered states are rather close in energy. For example, the interaction between isospins on nearest-neighbor rungs in the ladder,  $J_A = \frac{1}{4} V_{\mathbf{n}, \mathbf{n}+\mathbf{f}_1}$ , calculated by substituting into Eq. (2) the unscreened Coulomb interactions between electrons, is 0.62 eV. This “antiferromagnetic” interaction favors a zigzag structure, like e.g., the one shown in Fig. 5(a). For this type of ordering  $\mathbf{Q} = (\pi/f_1, \pi/f_2)$ . On the other hand, the interaction between the isospins on the nearest rungs of two neighboring ladders,  $J_F = \frac{1}{4} V_{\mathbf{n}, \mathbf{n}+\mathbf{f}_2} = -0.54$  eV, is “ferromagnetic.” The ferromagnetic interaction favors the structure shown in Fig. 5(b), in which electrons occupy with higher probability one chain of each ladder. For this chain structure  $\mathbf{Q} = 0$ .<sup>7</sup> If one would take into account only the Ising interactions between the

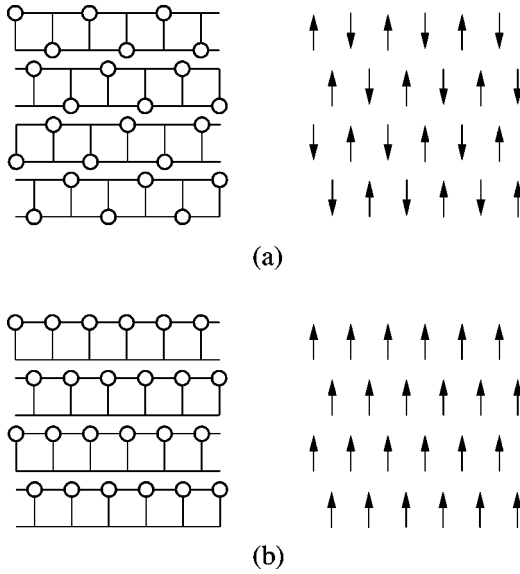


FIG. 5. Two charge ordered states: zigzag (or antiferroelectric) ordering with the doubling of the unit cell in the directions  $a$  and  $b$  (a) and the chainlike (ferroelectric) structure (b). The left part of each picture shows the distribution of the electronic density, while the right part shows the corresponding ordering of isospins.

neighboring rungs, then for  $J_A > |J_F|$  the energy of the zigzag structure is lower than that of the chain structure.

Since the difference between  $J_A$  and  $|J_F|$  is relatively small, the long-range interactions, the screening, and the coupling of the isospins to the lattice are important for determining the nature of the ordered state. As the precise calculation of the interactions between the isospins is very difficult, one can discriminate between different charge-ordered states on the basis of the available experimental data. Unfortunately the low-temperature crystal structure of sodium vanadate still remains unknown and the existing interpretations of the recent crystallographic data are controversial.<sup>15–17</sup> The most recent experiments on the anomalous x-ray scattering are consistent with some kind of the zigzag ordering, but not with the chain structure.<sup>18</sup> The zigzag structure, shown Fig. 5, is also consistent with the doubling of the lattice periodicity in the  $a$  and  $b$  directions, observed in  $\text{NaV}_2\text{O}_5$  below  $T_c$ , whereas the chainlike ordering [see Fig. 5(b)] does not result in an increase of the lattice period. Furthermore, the shape of the anomaly in the temperature dependence of the dielectric constant near  $T_c$  indicates that the ordering of electric dipoles below  $T_c$  in the  $a$  direction is of the antiferroelectric type,<sup>19–21</sup> which corresponds to a zigzag ordering, while the chain structure corresponds to a ferroelectric state. On the basis of all these data, we chose in what follows the zigzag structure as the ground state of  $\text{NaV}_2\text{O}_5$ .

To summarize this section, our model of the charge ordering in sodium vanadate implies the existence of a soft antiferroelectric mode in the spectrum of charge excitations of sodium vanadate.

#### IV. ISOSPIN EXCITATIONS AND OPTICAL ABSORPTION

The isospin excitations discussed in the previous section can be excited by applying an electric field in the direction of

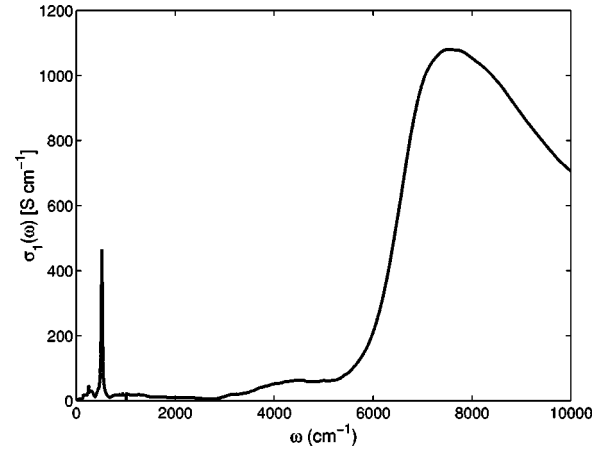


FIG. 6. The frequency dependence of the real part of the optical conductivity of  $\text{NaV}_2\text{O}_5$  at 300 K in the midinfrared range (courtesy of Professor D. van der Marel Refs. 23 and 24).

the rungs ( $a$  direction). Within the isospin model the interaction with such a field,  $E_a(t)$ , is described by the Hamiltonian

$$H_{int} = elE_a(t) \sum_{\mathbf{n}} T_{\mathbf{n}}^z, \quad (15)$$

where  $l \approx a/3$  is the length of the rung. Then the contribution to the dielectric susceptibility of the electrons occupying the  $d_{xy}$  orbitals on the vanadium sites is

$$\chi_a(\omega, \mathbf{q}) = -C \langle \langle T^z | T^z \rangle \rangle_{\omega, \mathbf{q}}, \quad (16)$$

where the constant  $C = 2e^2 l^2 / abc$ ,  $a, b$ , and  $c$  being the lattice constants of the high-temperature unit cell, and the retarded Green function  $\langle \langle T^z | T^z \rangle \rangle_{\omega, \mathbf{q}}$  is given by Eq. (9).

The frequency dependence of the dielectric susceptibility was measured by optical absorption.<sup>23,25,30</sup> Its imaginary part shows a rather broad peak at energy  $\sim 0.9$  eV (see Fig. 6), which was assigned in Ref. 23 to bonding-antibonding excitations of electrons on rungs. In our model this peak corresponds to the photoexcitation of the isospin excitation with  $\mathbf{q} = 0$  [see Eq. (9)].

We note that the observed large value of  $E_{\mathbf{q}=0}$  is additional evidence against the chainlike ordering [see Fig. 5(b)]. As was discussed in Sec. III, for the chain structure the bottom of the exciton band would be at  $\mathbf{q} = 0$ , and the strong peak in the optical absorption would be observed at an energy much lower than 0.9 eV. On the other hand, for the zigzag structure, shown in Fig. 5(a), the excitation with  $\mathbf{q} = 0$  lies far from the bottom of the exciton band, located at  $\mathbf{Q} = (\pi/f_1, \pi/f_2)$ . Therefore its energy  $E_{\mathbf{q}=0}$  may be rather large ( $\sim 2t_{\perp}$ ).

A remarkable feature of the optical absorption spectrum of sodium vanadate is the low-energy shoulder of the main peak at  $8000 \text{ cm}^{-1}$ , which extends all the way down to  $\sim 3000 \text{ cm}^{-1}$  (see Fig. 6). Furthermore, at lower frequencies there is another broad absorption band stretching from  $\sim 100 \text{ cm}^{-1}$  up to  $\sim 1500\text{--}2000 \text{ cm}^{-1}$  with a maximum at  $\sim 300 \text{ cm}^{-1}$ .<sup>23–25</sup> A very broad peak with a maximum at  $600 \text{ cm}^{-1}$  is also observed in Raman scattering.<sup>25–27</sup> The

large width of these peaks, as well as a number of Fano resonances observed in the far-infrared absorption spectrum,<sup>23–25</sup> indicate the presence of a broad continuum of low-energy excitations in sodium vanadate, which covers, practically, the entire midinfrared range of frequencies. In the remainder of this section and in Sec. V, we will investigate several explanations for this continuum.

The low-energy continuum, observed both above and below  $T_c$ , can, in principle, be due to the simultaneous photoexcitation of several isospin excitations lying close to the bottom of the exciton band. To describe such processes one has to go beyond the RPA. Then the one-exciton states are mixed with the states containing three, five, and more excitons. However, since the number of excitons created in the photoabsorption is odd, the momentum conservation does not allow all of them simultaneously to have low energy. Thus the pure exciton continuum should begin at rather high energies and cannot account for the mid-infrared continuum in sodium vanadate.

To substantiate the point that the isospin excitations alone cannot give rise to the observed low-energy optical absorption, we consider an isolated vanadium ladder with the isospin Hamiltonian:

$$H_T = -2t_\perp \sum_n T_n^x + V \sum_n T_n^z T_{n+1}^z.$$

For open boundary conditions, this Hamiltonian can be diagonalized exactly. To this end we first perform a rotation around the  $y$  axis in the isospin space (cf. the Appendix). The resulting Hamiltonian is diagonalized by transforming the isospins to fermions (using the Jordan-Wigner transformation) and then applying a Bogoliubov transformation.<sup>33</sup> The exact dispersion of the Fermionic excitations reads

$$E_q = \sqrt{\left(2t_\perp + \frac{V}{2}\cos q\right)^2 + \left(\frac{V}{2}\sin q\right)^2},$$

with  $q$  a quantum number that follows from a transcendental equation,<sup>33</sup> and which lies in the interval  $0 < q < \pi$ . Thus the isospin gap is given by

$$\Delta = E_\pi = \left|2t_\perp - \frac{V}{2}\right|.$$

The oscillator strength of a  $n$ -exciton state ( $n$  odd) may now be expressed in terms of the ground-state expectation value of strings of Fermi operators. The latter may be evaluated using Wick's theorem which results in determinants of matrices with components that follow from the Bogoliubov transformation coefficients. For the one- and three-exciton states, this calculation has been performed explicitly in Ref. 34. Using these results, we find for a ladder of  $N=70$  rungs and  $2t_\perp=0.7$  eV the absorption spectrum plotted in Fig. 7. The narrow peak is due to the single-exciton absorption. The absorption above the main peak is due to the photoexcitation of three excitons. This process contributes to the broad high-energy wing of the main absorption peak observed in sodium vanadate.<sup>23</sup> The small oscillator strength at frequencies below the frequency of the main peak is due to the one-exciton

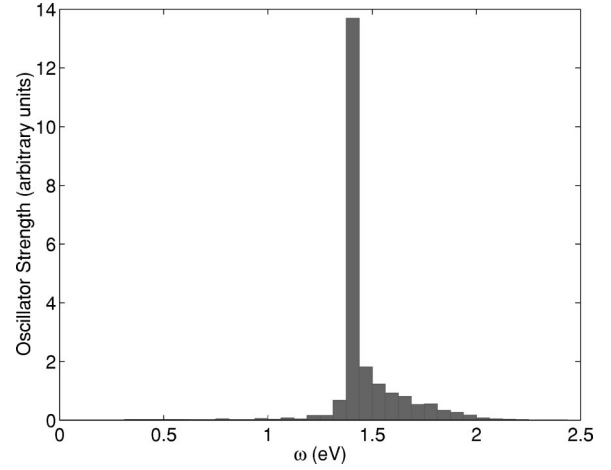


FIG. 7. The oscillator strength for an isolated two-leg ladder of  $N=70$  rungs with a very small value of the isospin gap at  $q=\pi$  (see explanations in the text). The narrow peak is due to the single exciton absorption. The absorption above the main peak is due to the simultaneous photoexcitation of three excitons. The very small oscillator strength for the frequencies below the frequency of the main peak is due to the one-exciton absorption and is a finite-size effect.

absorption and is a finite-size effect (breaking of the momentum selection rule). For small photon frequencies the absorption due to the five-exciton states is negligible due to the small phase volume of these states. We mention that to calculate Fig. 7, we have deliberately chosen a very small value of the isospin gap,  $\Delta = 10^{-4}$  eV, in order to show that, even for  $\Delta \rightarrow 0$ , one cannot obtain a low-energy absorption in the pure isospin model.

## V. OPTICAL ABSORPTION AT LOW ENERGIES

It is natural to identify the broad absorption band stretching from  $\sim 100$   $\text{cm}^{-1}$  up to  $\sim 1500$   $\text{cm}^{-1}$  with the photoexcitation of one phonon and two spinons.<sup>35</sup> In this (Lorenzana-Sawatzky) mechanism the phonon provides a coupling of the spin excitations to light and takes care of the wave vector conservation. On the other hand, the width of the absorption band is mainly determined by the width of the two-spinon continuum,<sup>36</sup> which for sodium vanadate is  $\pi J \approx 1200$   $\text{cm}^{-1}$  (here  $J$  is the exchange constant between the nearest-neighbor spins in the ladders).

In Refs. 23 and 24 it was suggested that the coupling between spin and charge degrees of freedom in the two-leg ladders enables the direct photoexcitation of two spinons (the so-called “charged magnon” mechanism). In our model, the corresponding diagram, describing the direct photoexcitation of spinons, is shown in Fig. 8(a): This process involves the creation of a virtual high-energy isospin excitation with  $\mathbf{q}=0$ , which then decays into two spinons. However, the coupling of the isospin excitation with zero wave vector to spinons is only nonzero if the system has a permanent electric dipole. In other words, the magnons have charge only if the ladders are ferroelectric, which would require the chain-like electronic ordering [cf. Fig. 5(b)] both above and below  $T_c$ . In Ref. 24 it was argued, however, that the direct photo-

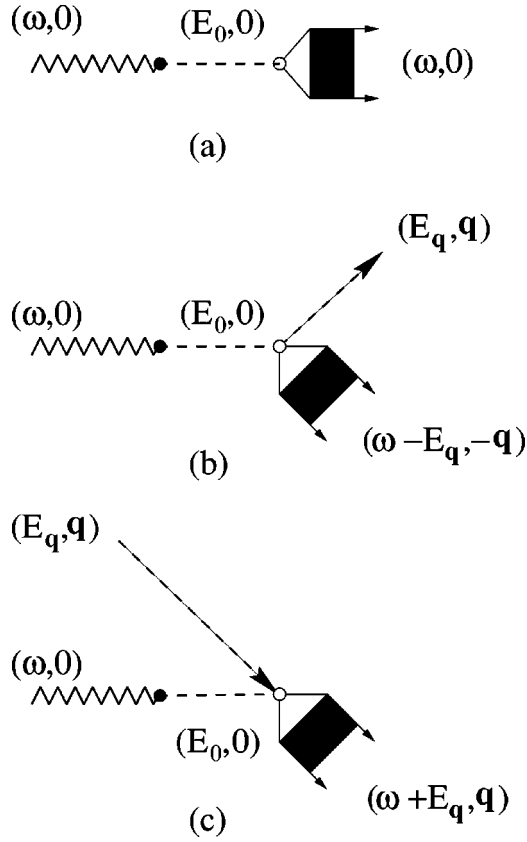


FIG. 8. Diagrams describing: (a) the “charged magnon” mechanism, (b) the photoexcitation of the two-spinon continuum and a low-energy exciton, and (c) the photoexcitation of the two-spinon continuum with the annihilation of a low-energy exciton. The wavy and dashed lines correspond to, respectively, a photon and a charge exciton, while the black square indicates the two-spinon continuum.

excitation of spinons is still possible in the disordered state due to local fluctuations of electric dipoles on the ladder rungs (which in that paper are treated as classical variables).

In any case, neither of the two mechanisms discussed above can explain the low-energy shoulder of the 0.9-eV peak, appearing above  $\omega > 3000 \text{ cm}^{-1}$ , because the maximal energy that can be carried by two spinons,  $\pi J$ , is relatively small. On the other hand, the isospin excitations introduced in Sec. III have a rather wide band and therefore can give rise to the observed shoulder: As was argued in Sec. III, the softening of the isospin excitations at the charge ordering temperature implies a bandwidth  $\sim 2t_{\perp}$ —otherwise the isospin gap  $\Delta$  cannot be small. However, for the zigzag ordering the isospin gap is indirect, and the low-energy optical absorption is only possible if other excitations carry away part of the wave vector (see Sec. IV). Thus, in principle, the shoulder can result from the photoexcitation of one isospin excitation and a phonon. Another possibility is photoexcitation of a three-particle continuum: two spinons and one low-energy isospin excitation. This mechanism is illustrated by the diagram in Fig. 8(b). This process also takes place via a virtual isospin excitation with zero wave vector and high energy  $E_0$ , which then decays into a low-energy isospin excitation with wave vector  $\mathbf{q}$  close to the bottom of the band,

$\mathbf{q} \sim \mathbf{Q}$ , and two spin excitations that carry the momentum  $-\mathbf{q}$ . Alternatively, a thermally excited isospin excitation can be annihilated in the process of optical absorption [see Fig. 8(c)].

In this paper we shall only consider the optical absorption that is accompanied by the photoexcitation of spins. This mechanism requires the coupling of *two* isospin excitations (one of high energy, another of low energy) to two spin excitations. In our model such a coupling naturally arises, because the spin exchange of electrons on neighboring rungs of a two-leg ladder cannot be separated from the exchange of their isospins (see Sec. II).

As an exact treatment of the spin-isospin model is not possible we use a number of approximations to calculate the optical absorption spectrum. First we note that the Hamiltonian of the spin-isospin interaction given by Eqs. (3), (5), and (6) can be written in the form

$$H_{ST} = H_{ST}^{(1)} + H_{ST}^{(2)} + H_{ST}^{(3)} = \sum_{\mathbf{n}} \mathcal{T}_{\mathbf{n}} \mathcal{S}_{\mathbf{n}},$$

where  $\mathcal{T}_{\mathbf{n}}$  contains all isospin operators:

$$\begin{aligned} \mathcal{T}_{\mathbf{n}} = & A(T_{\mathbf{n}}^x T_{\mathbf{n}+\mathbf{f}_1}^x + T_{\mathbf{n}}^y T_{\mathbf{n}+\mathbf{f}_1}^y) + A' T_{\mathbf{n}}^z T_{\mathbf{n}+\mathbf{f}_1}^z \\ & + B(T_{\mathbf{n}+\mathbf{f}_2}^z - T_{\mathbf{n}+\mathbf{f}_1-\mathbf{f}_2}^z), \end{aligned} \quad (17)$$

and

$$\mathcal{S}_{\mathbf{n}} = \mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}+\mathbf{f}_1}.$$

Although in our model the spin dynamics is inseparable from the dynamics of the isospins, we may obtain a “pure spin Hamiltonian” by treating the isospin operators in  $H_{ST}$  within the mean-field approximation,

$$H_S = \sum_{\mathbf{n}} J_{\mathbf{n}, \mathbf{n}+\mathbf{f}_1} (\mathbf{S}_{\mathbf{n}} \cdot \mathbf{S}_{\mathbf{n}+\mathbf{f}_1}), \quad (18)$$

where the effective spin-exchange constant is obtained by the thermal average of  $\mathcal{T}_{\mathbf{n}}$  over the state of the isospin system,

$$J_{\mathbf{n}, \mathbf{n}+\mathbf{f}_1} = \langle \mathcal{T}_{\mathbf{n}} \rangle_{H_T}.$$

As was already discussed in Sec. II, the thus obtained spin-exchange constant depends on temperature and becomes alternating along the spin chains below  $T_c$ . Since according to our assumption the charge ordering is mainly driven by the pure isospin Hamiltonian  $H_T$ , we neglect the effect of the spin-isospin interactions on the state of the isospin system. The remaining part of the spin-isospin Hamiltonian (the residual interaction) describes the scattering of isospin excitations on spin excitations. This scattering gives rise to the low-energy absorption and will be treated as a perturbation.

In this paper we consider the optical absorption only above  $T_c$  (i.e., no charge ordering and no spin gap). Furthermore, the isospin excitations are treated as bosons. In particular, the operator

$$T_{\mathbf{q}}^z = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} e^{-i\mathbf{q}\cdot\mathbf{r}_{\mathbf{n}}} T_{\mathbf{n}}^z$$



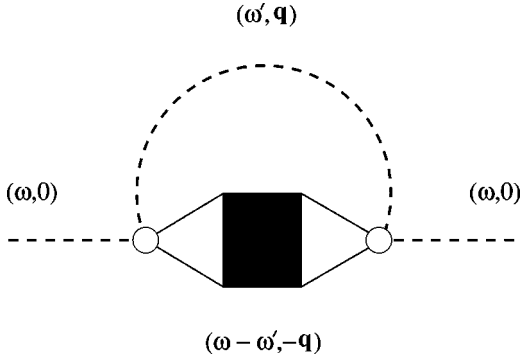


FIG. 9. The diagram describing the correction to the Green function of the isospin excitation due to scattering on the spin excitations. This correction gives rise to low-energy optical absorption.

annihilates the isospin excitation with the wave vector  $\mathbf{q}$  and creates such an excitation with the wave vector  $-\mathbf{q}$

$$T_{\mathbf{q}}^z \sim \sqrt{\frac{t_{\perp} M}{E_{\mathbf{q}}}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}).$$

The coefficient in the right-hand side of the last equation was found by comparison of this equation with the Green function Eq. (A9).

Since the operator  $\mathcal{T}_{\mathbf{n}}$  [see Eq. (17)] contains products of two isospin operators, it either results in the creation and annihilation of two isospin excitations, or in the scattering of the isospin excitation. In particular, if one of the isospin excitations has zero wave vector (as is the case in the optical absorption), then

$$\mathcal{T}_{\mathbf{q}} \sim g_{\mathbf{q}} \frac{t_{\perp} M}{\sqrt{E_0 E_{\mathbf{q}}}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}) (b_0^{\dagger} + b_0),$$

where  $g_{\mathbf{q}}$  is the coupling constant.

To lowest order in the residual spin-isospin interaction, the Green function of the isospin excitation obtains the correction shown in Fig. 9, which leads to the low-energy optical absorption described by the diagrams in Figs. 8 (b) and (c). The corresponding contribution to the imaginary part of the dielectric susceptibility is

$$\begin{aligned} \Delta \chi_a''(\omega, 0) = & \frac{K}{N} \sum_{\mathbf{q}} \frac{|g_{\mathbf{q}}|^2}{E_0 E_{\mathbf{q}}} \\ & \times \left[ \chi_S''(\omega - E_{\mathbf{q}}, -\mathbf{q}) \left( \coth \frac{E_{\mathbf{q}}}{2T} - \coth \frac{(E_{\mathbf{q}} - \omega)}{2T} \right) \right. \\ & \left. + \chi_S''(\omega + E_{\mathbf{q}}, \mathbf{q}) \left( \coth \frac{E_{\mathbf{q}}}{2T} - \coth \frac{(E_{\mathbf{q}} + \omega)}{2T} \right) \right]. \end{aligned} \quad (19)$$

Here, the first term in square brackets is due to photoexcitation of one low-energy exciton plus two spinons [see Fig. 8(b)], while the second term describes annihilation of a ther-

mally excited low-energy excitation, accompanied by the creation of two spin excitations [see Fig. 8(c)]. In Eq. (19) we have defined

$$K = \frac{1}{abc} \left( \frac{2elt_{\perp}^2 M^2}{E_0^2 - \omega^2} \right)^2,$$

while  $\chi_S(\omega, \mathbf{q}) = \chi_S(\omega, q_1)$  is the susceptibility of the Heisenberg spin- $\frac{1}{2}$  chain,

$$\chi_S(\omega, q_1) = i \int_0^{\infty} dt e^{i\omega t - i q_1 n} \langle [\mathcal{S}_n(t), \mathcal{S}_0(0)] \rangle_{H_S} \quad (20)$$

(here  $q_1$  is the wave vector in the chain direction measured in units of  $1/b$ ). Since no exact expression for this susceptibility is known that holds for all values of  $q, \omega$ , and  $T$ , we calculate it by substituting the Heisenberg model by the renormalized  $XY$  model, which is equivalent to a half filled chain of spinless fermions with the dispersion  $\varepsilon(k) = -pJ \cos k$ , where  $p = 1 + 2/\pi$ .<sup>31</sup> Then

$$\mathcal{S}_n \rightarrow -\frac{p}{2} (c_{n+1}^{\dagger} c_n + c_n^{\dagger} c_{n+1}),$$

and

$$\begin{aligned} \chi_S''(\omega, q) = & \frac{p^2}{4} \int_{-\pi}^{\pi} dk \delta(\omega + \varepsilon_k - \varepsilon_{k+q}) \cos^2 \left( k + \frac{q}{2} \right) \\ & \times \left[ \tanh \frac{\varepsilon_{k+q}}{2T} - \tanh \frac{\varepsilon_k}{2T} \right]. \end{aligned}$$

According to our assumption, the isospin excitations only are soft in a small vicinity of  $q_1 = \pi$ . Then the wave vector of the spin excitations in the low-energy continuum is also close to  $\pi$ , in which case the analytical expression for the imaginary part of the spin susceptibility is

$$\chi_S''(\omega, \pi) = \theta(\Omega^2 - \omega^2) \frac{p^2}{\Omega} \sqrt{1 - \left( \frac{\omega}{\Omega} \right)^2} \tanh \frac{\omega}{4T}. \quad (21)$$

Here,  $\Omega = 2pJ$  is the bandwidth of the spinless fermions, which corresponds to the maximal energy of the two-spinon excitation in the Heisenberg model.

Figure 10 shows the comparison of the results of the analytical calculation of optical conductivity,  $\sigma_1(\omega) = \omega \chi_a''(\omega, 0)$ , using Eqs. (19) and (21), and the room-temperature measurements.<sup>23,24</sup> Roughly speaking, the optical absorption spectrum due to the three-particle continuum measures the density of the isospin excitations. Since the spectrum of these excitations stretches from very low energies near the bottom of the band at  $\mathbf{q} = \mathbf{Q}$  up to the energies of the order of  $2t_{\perp}$ , a (relatively small) optical absorption occurs at all frequencies between  $\Delta$  and  $E_0$ , in good agreement with experiments. The optical absorption due to the three-particle continuum continuously grows with the photon energy, as the available phase volume of the excitations increases. This mechanism is therefore not effective at low frequencies, where the photoexcitation of a phonon and a phonon plus two spinons are two dominant processes. This

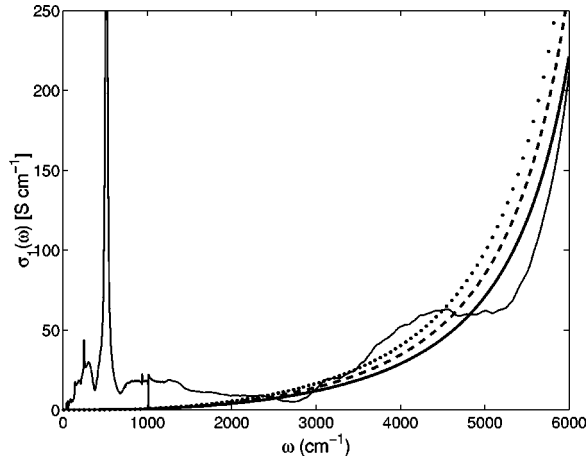


FIG. 10. Comparison of the results of the analytical calculation of the optical absorption spectrum of sodium vanadate for  $T = 300$  K (thick solid line),  $T = 150$  K (dashed line), and  $T = 50$  K (dotted line) with the experimental results obtained at room temperature (Refs. 23 and 24) (thin line).

explains the disagreement between the analytical and experimental curves at  $\omega < 2000$   $\text{cm}^{-1}$ .

We did the calculations for three values of temperature  $T = 300$  K (thick line),  $T = 150$  K (dashed line), and  $T = 50$  K (dotted line). The optical absorption slightly increases, when temperature goes down, which is related to the increase of the number of available two-spinon excitations. A similar increase was also observed experimentally.<sup>23,24</sup> (To avoid misunderstanding, we stress that in this paper we study the optical absorption in the high-temperature phase, i.e., in the absence of the charge ordering and the spin gap).

Though the value of the isospin gap, in principle, depends on  $T$ , in our analytical calculations we used  $\Delta = 0$ , since the dependence of  $\sigma_1(\omega)$  on the value of the isospin gap is very weak for small  $\Delta$ : For instance, the curves for  $\Delta = 0$  and  $\Delta = 300$  K are barely distinguishable, the main changes taking place at low frequencies, where the analytically calculated optical conductivity is very small. This is related to the fact that the typical energy of the excitation is of the order of the photon energy,  $\sim \hbar\omega$ , since the phase volume of these excitations grows with their energy.

Finally, we note that, in agreement with our theory, this continuum is only experimentally observed when the electric field is directed along the ladder rungs (along **a**).

## VI. DISCUSSION AND CONCLUSIONS

In this paper we proposed an explanation of the low-energy absorption observed in sodium vanadate. We argued that the spectrum of the low-energy excitations in sodium vanadate should contain an antiferroelectric mode, which softens at the charge ordering temperature. This mode is an exciton—the itinerant bonding-antibonding excitation on the ladder rungs, which we describe by isospin Hamiltonian. The exciton bandwidth, determined by the Coulomb interactions between electrons on different rungs, has to be  $\sim 2t_{\perp}$  to make the gap in the spectrum of these excitations small. Since the gap of the antiferroelectric mode is indirect, it is

impossible to excite a single low-energy exciton by the optical absorption.

The antiferroelectric mode is strongly coupled to spins: A pure spin exchange does not exist—the exchange of spins necessarily involves the exchange of isospins. One manifestation of this coupling is the temperature dependence of the effective spin-exchange constants. Below the charge ordering temperature the spin-exchange constants alternate along ladders, which opens a spin gap. The coupling between the antiferroelectric mode and spins also gives rise to the photoexcitation of a three-particle continuum (one low-energy exciton and two spinons). The importance of mixed spin-isospin excitations was also noted in numerical studies of the optical absorption in the spin-isospin model.<sup>37</sup> Our calculation shows that this process may well account for the broad bands in the optical absorption spectrum of sodium vanadate found in the whole range of midinfrared frequencies.

We also note that below  $T_c$ , the quasimomentum conservation allows for the optical excitation of a single low-energy excitation, as the increase of the lattice period folds these modes into the zone center. Indeed, both in optical absorption<sup>32</sup> and Raman spectra,<sup>27</sup> several lines have been observed whose intensity shows an anomalous temperature dependence.

Thus the spin-isospin model allows us to explain qualitatively the main experimental facts on sodium vanadate, i.e., the charge ordering, the spin gap opening, and the low-energy absorption. The main difficulty of this model is to explain the low value of the charge ordering temperature. One possibility is the proximity to a quantum critical point, at which the energy of the electron excitation on a rung,  $2t_{\perp} \sim 0.7$  eV, is exactly compensated by a large band width of the isospin excitations. The proximity to the quantum critical point may also be responsible for the strong dependence of  $T_c$  on the hydrostatic pressure observed in sodium vanadate.<sup>38,39</sup> Both the hopping amplitude  $t_{\perp}$  and the amplitudes of the dipolar interactions between the rungs,  $V_{nm}$ , increase under pressure. However,  $t_{\perp}$ , which involves the overlap of electronic wave functions, depends on the distances between ions more strongly than  $V_{nm}$ . Since the hopping amplitude tends to disorder the system, the transition temperature decreases under pressure. The proximity to a quantum critical, however, requires a fine tuning of the model parameters (the electron hopping and the Coulomb interactions between electrons). Another possibility, the frustration of the Ising interactions due to the relative shifts between neighboring ladders, will be discussed in detail elsewhere.

In conclusion, in sodium vanadate the electronic charge dynamics seems to play an important role, and the coupling between the charge and spin degrees of freedom is crucial in understanding the properties of this material. Finally, we note that a similar spin-isospin model could be used to describe the interplay between the charge and antiferromagnetic ordering in the quasi-two-dimensional organic system  $\kappa$ -(BEDT-TTF)<sub>2</sub>X (see, e.g., Refs. 40 and 41), in which the role of the V rungs is played by dimers of BEDT-TTF molecules.

## ACKNOWLEDGMENTS

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## APPENDIX: SPECTRUM OF ISOSPIN EXCITATIONS IN RPA

In this Appendix we find the spectrum of isospin excitations both in the disordered and ordered phases. Above  $T_c$ ,  $M_n^z=0$  and  $M_n^x=M \neq 0$ . It is convenient to perform a rotation in the isospace,

$$\begin{bmatrix} T_n^x \\ T_n^y \\ T_n^z \end{bmatrix} \rightarrow \begin{bmatrix} T_n'^x \\ T_n'^y \\ T_n'^z \end{bmatrix} = \begin{bmatrix} -T_n^z \\ +T_n^y \\ +T_n^x \end{bmatrix}. \quad (\text{A1})$$

In the rotated basis  $\langle T_n'^z \rangle = M$  and the Hamiltonian has the form

$$H_T = -2t_\perp \sum_n T_n'^z + \frac{1}{2} \sum_{nm} V_{nm} T_n'^x T_m'^x. \quad (\text{A2})$$

We then use the equations of motion for the operators  $T_n'^\pm = T_n'^x \pm iT_n'^y$ :

$$\pm i\dot{T}_n'^\pm = 2t_\perp T_n'^\pm + \frac{1}{2} \sum_m V_{nm} T_n'^z (T_m'^+ + T_m'^-), \quad (\text{A3})$$

in which we substitute  $T_n^z$  by its average value  $M$ . This approximation, equivalent to the decoupling of the Green functions containing more than two isospin operators,<sup>42,43</sup> gives a closed system of equations,

$$\begin{cases} \left[ \omega - 2t_\perp - \frac{M}{2} V(\mathbf{q}) \right] \langle \langle T'^+ | T'^- \rangle \rangle \\ - \frac{M}{2} V(\mathbf{q}) \langle \langle T'^- | T'^- \rangle \rangle = 2M, \\ \frac{M}{2} V(\mathbf{q}) \langle \langle T'^+ | T'^- \rangle \rangle \\ + \left[ \omega + 2t_\perp + \frac{M}{2} V(\mathbf{q}) \right] \langle \langle T'^- | T'^- \rangle \rangle = 0 \end{cases} \quad (\text{A4})$$

for the retarded Green functions  $\langle \langle A|B \rangle \rangle \equiv \langle \langle A|B \rangle \rangle_{\omega, \mathbf{q}}$ , defined by

$$\langle \langle A|B \rangle \rangle_{\omega, \mathbf{q}} = -i \int_0^\infty dt e^{i(\omega + i\delta)t} \sum_n e^{-i\mathbf{q} \cdot \mathbf{x}_n} \langle [A, B] \rangle. \quad (\text{A5})$$

In this way we get

$$\begin{cases} \langle \langle T'^+ | T'^- \rangle \rangle_{\omega, \mathbf{q}} = 2M \frac{\left[ \omega + 2t_\perp + \frac{M}{2} V(\mathbf{q}) \right]}{\omega^2 - E_q^2 + i\delta \text{sgn} \omega}, \\ \langle \langle T'^- | T'^- \rangle \rangle_{\omega, \mathbf{q}} = -\frac{M^2 V(\mathbf{q})}{\omega^2 - E_q^2 + i\delta \text{sgn} \omega}. \end{cases} \quad (\text{A6})$$

Furthermore,

$$\begin{cases} \langle \langle T'^- | T'^+ \rangle \rangle_{\omega, \mathbf{q}} = \langle \langle T'^+ | T'^- \rangle \rangle_{-\omega, \mathbf{q}}, \\ \langle \langle T'^+ | T'^+ \rangle \rangle_{\omega, \mathbf{q}} = \langle \langle T'^- | T'^- \rangle \rangle_{\omega, \mathbf{q}}. \end{cases} \quad (\text{A7})$$

The Green functions have poles at (plus/minus) the energy of the isospin excitation with wave vector  $\mathbf{q}$ ,

$$E_q = \sqrt{2t_\perp [2t_\perp + M V(\mathbf{q})]}. \quad (\text{A8})$$

The band of isospin excitations has its bottom at the wave vector  $\mathbf{q} = \mathbf{Q}$ , where  $V(\mathbf{q})$  has its minimum.

Combining Eqs. (A6) and (A7) we obtain

$$\langle \langle T^z | T^z \rangle \rangle_{\omega, \mathbf{q}} = \langle \langle T'^x | T'^x \rangle \rangle = \frac{2t_\perp M}{(\omega^2 - E_q^2 + i\delta \text{sgn} \omega)}. \quad (\text{A9})$$

In the ordered phase below  $T_c$  we introduce on each site  $\mathbf{n}$  an angle  $\phi_n$  by

$$\begin{cases} M_n^x = M_n \cos \phi_n, \\ M_n^z = M_n \sin \phi_n, \end{cases} \quad (\text{A10})$$

where we used the original basis. Then the first of the self-consistency equations, Eq. (12), reads

$$2t_\perp \sin \phi_n + \cos \phi_n \sum_m V_{nm} M_m \sin \phi_m = 0. \quad (\text{A11})$$

We now choose the basis in the isospin space, such that the  $z$  axis is oriented along  $\langle \mathbf{T}_n \rangle$ ,

$$\begin{cases} T_n'^x = \sin \phi_n T_n^x - \cos \phi_n T_n^z, \\ T_n'^y = T_n^y, \\ T_n'^z = \cos \phi_n T_n^x + \sin \phi_n T_n^z. \end{cases} \quad (\text{A12})$$

Then  $\langle T_n'^z \rangle = M_n$  and  $\langle T_n'^x \rangle = \langle T_n'^y \rangle = 0$ .

Using Eq. (A11) the linearized equations of motion for  $T'^\pm$  can be written in the form

$$\begin{aligned} \pm i\dot{T}_n'^\pm &= \frac{2t_\perp}{\cos \phi_n} T_n'^\pm + \frac{1}{2} M_n \cos \phi_n \\ &\times \sum_m V_{nm} \cos \phi_m (T_m'^+ + T_m'^-). \end{aligned} \quad (\text{A13})$$

Both for the zigzag and the chain ordering,

$$\phi_n = e^{i\mathbf{Q} \cdot \mathbf{x}_n} \phi, \quad (\text{A14})$$

and  $|\phi_n| = \phi$ . Then, Eq. (A11) gives  $M_n = M$  and

$$M = \frac{2t_{\perp}}{\cos \phi |V(\mathbf{Q})|}. \quad (\text{A15})$$

Furthermore, from Eq. (A13) we see that the Green functions in the ordered phase can be obtained from those above  $T_c$  by substituting  $2t_{\perp}$  by  $2t_{\perp}/\cos \phi$  and  $V(\mathbf{q})$  by  $V(\mathbf{q})\cos^2 \phi$ , e.g.,

$$\langle\langle T'^+ | T'^- \rangle\rangle_{\omega, \mathbf{q}} = 2M \frac{\left( \omega + \frac{2t_{\perp}}{\cos \phi} + \frac{M}{2} \cos^2 \phi V(\mathbf{q}) \right)}{\omega^2 - E_{\mathbf{q}}^2 + i \delta \text{sgn} \omega}, \quad (\text{A16})$$

where the energy of the isospin excitations is given by

$$E_{\mathbf{q}} = \frac{2t_{\perp}}{\cos \phi} \sqrt{1 - \cos^2 \phi^2 \frac{V(\mathbf{q})}{V(\mathbf{Q})}}. \quad (\text{A17})$$

Since below  $T_c$ ,  $0 < \cos \phi < 1$ , the isospin gap in the ordered phase,  $\Delta = E_{\mathbf{Q}} = 2t_{\perp} \tan \phi > 0$ . The dispersion relations Eqs. (A8) and (A17) can be combined to give Eq. (10) valid both above and below  $T_c$ .

Using Eq. (A11), one can check that the Green functions of  $T'^z$  and any other operator vanish. Then,  $\langle\langle T^z | T^z \rangle\rangle_{\omega, \mathbf{q}} = \cos^2 \phi \langle\langle T'^x | T'^x \rangle\rangle$ , so that below  $T_c$ ,

$$\langle\langle T^z | T^z \rangle\rangle_{\omega, \mathbf{q}} = \frac{(2t_{\perp})^2}{|V(\mathbf{Q})|} \frac{1}{(\omega^2 - E_{\mathbf{q}}^2 + i \delta \text{sgn} \omega)}. \quad (\text{A18})$$

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